

ACID CATALYZED DEPOLYMERIZATION OF COAL UNDER MILD CONDITIONS WITH SUPERACID HF/BF₃

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1. INTRODUCTION

Acid-catalyzed coal depolymerization has been widely studied as a way to liquefy coal under milder conditions¹⁻⁴. However, it is usually very difficult to recover completely the acid catalyst from solids or products. HF/BF₃, which has been recognized as a Bronsted/Lewis superacid catalyst for Friedel-Crafts reactions: isomerization and separation of m-xylene, and formylation of aromatic compounds on an industrial scale (Mitsubishi Gas Chemical Co., Ltd.). HF/BF₃ mixtures are fully recoverable from the product by distillation only, and can be reused, because their boiling points are very low (HF: 19.9°C, BF₃: -101°C). Olah studied coal liquefaction using the HF-BF₃-H₂ system and HF-BF₃-isopentane⁵. We also reported that HF and HF/BF₃ in the presence of toluene depolymerized coal more efficiently at 100-150°C through the acid-catalyzed transalkylation reaction of coal⁶.

In the present study, solubilization of coals of different rank were carried out at 50-150°C in order to evaluate recyclable superacid HF/BF₃ as catalyst for efficient depolymerization of coal of different rank via an ionic reaction. The depolymerization of coals in the acid-catalyzed reaction process was considered in terms of the chemical structure of coals and behaviors of oxygen containing functional groups.

Table 1 Elemental analyses of the treated coals.

Run	Elemental analyses (wt%, daf base)				ash (wt%)
	C	H	N	O _{air}	
Yallourn	65.6	4.6	0.6	29.20	1.3
Taiheiyō	73.3	6.4	1.2	19.1	13.7
Miike	82.0	6.7	1.2	10.1	14.7

2. EXPERIMENTAL

Yallourn lignite, Taiheiyō subbituminous and Miike bituminous coal were used, ground to a diameter of 0.25mm less and dried in a vacuum at 110°C for 24h (Table 1). The liquefaction was carried out in a hastelloy-C microautoclave of 100 ml capacity. Coal (5 g) and toluene or isopentane (20ml) were placed in the dry ice-methanol cooled autoclave. First, the reactor of autoclave was evacuated by vacuum pump; then the HF (0.582 g/g-coal) and BF₃ (0.219 g/g-coal) were introduced to the coal-solvent slurry while dry ice-methanol cooling continued. Gaseous hydrogen (5.1 MPa) was introduced to autoclave after BF₃ when instead of toluene or isopentane. The autoclave was then heated to 50-150°C at a heating rate of 1.5°C/min for 3 h under autogenous pressure with vigorous stirring. After the reaction, gaseous HF/BF₃, solvent and volatile fraction from toluene in the autoclave were depressurized and absorbed into ice-water at 90-110°C under flowing nitrogen gas (100-150 mL/min) with stirring (300rpm) for 2h. The contents of the autoclave were slowly poured into cool water, and then were gradually neutralized with an cool aqueous solution (5 wt%) of Na₂CO₃. The products were filtered and washed in water with sonication. Washing with an aqueous methanol solution (30-50 vol%) was repeated 3 times in order to remove small

amount of neutralized product NaF and dimer of toluene. The solid product was vacuum-dried at 110°C for 24h. Reaction conditions are summarized in Table 2. Calculation to obtain the yield of solubles and weight increase has been described in detail elsewhere⁸.

The products were extracted with benzene, THF and pyridine in a sequential Soxhlet extractor. Oxygen-containing functional groups were determined by the method of Hatami et al. This determination has been described in detail elsewhere⁹.

The ¹³C-CP/MAS solid-state NMR spectra were measured with a chemagnetics at 75.58 MHz. The following operating parameters were used: a spectral width of 30 kHz, a 90 proton pulse of 5 μs, an acquisition time of 34.130 ms, a pulse repetition time of 4 s and an accumulation of 4000 scans.

3. RESULTS AND DISCUSSION

3.1 Effects of reaction temperature

The effects of reaction temperature on coals solubilization in the presence of HF/BF₃ (7 mol%) are shown in Figure 1. The reaction at even 50°C showed higher extractability than original coals. The reaction at 100°C greatly increased extractability, especially Miike bituminous coal could solubilize almost completely. The reaction at 150°C resulted in high extractability as described. Pyridine soluble yield in the treated coals at the lower reaction temperature of 50 and 100 °C was increased with increasing of carbon content in coal. However, the extractability of product from any coal was not changed at the reaction temperature of 150°C.

3.2 Effects of stabilizer

The extractability of the products treated with different kinds of stabilizer are shown in Figure 2. Extractability of products from Yallourn lignite depend very much upon the kinds of stabilizer. Although it can solubilize nearly completely by the reaction with toluene isopentane and hydrogen showed lower extractability such as 49 and 20 wt%, respectively. Differences of extractability in the case of Taiheiyō subbituminous coal was smaller than Yallourn lignite. And the products from Miike bituminous coal was not significantly changed with kind of stabilizer.

3.3 Oxygen containing functional groups

The distribution of oxygen-containing functional groups in the original coals and the treated coals is summarized in Table 3. Oxygen-containing functional groups were divided into 4 groups(carboxylic, hydroxyl, carbonyl group and Orest). Orest is mostly ascribed to ether groups such as Ar-CH₂-O-R, Ar-O-Ar and Ar-O-R. Most of the oxygen-containing functional groups decreased after the reaction. Decreasing of ether bonds, carboxylic and hydroxyl groups were increased with increasing of reaction temperature. This highly deoxygenation during reaction at 150°C would be cause of high extractability of products. The reaction with isopentane under HF/BF₃ at 150 °C retained more hydroxyl groups and ether bond in the products than did the reaction with toluene, indicating that these oxygen containing functional groups remained restricted extractability, leading that lower coal depolymerization. In contrast, Miike bituminous coal inherently have small amount of oxygen containing functional groups, and their decreasing after reaction was substantially small, therefore behaviours of oxygen containing functional groups in Miike coal did not contribute the solubilization reaction.

These results indicated that Miike bituminous coal comparatively easy to produce highly soluble products even at any reaction conditions because of small amount of oxygen containing functional groups. In contrast, Yallourn lignite which have more amount of their functional groups and its content in products depend on the reaction condition such as kind of stabilizer and reaction temperature.

3.4 CP/MAS-¹³C NMR spectra

Table 4 summarizes the carbon distributions of original coals and treated coal from the reaction with HF/BF₃ under gaseous hydrogen. The carbon atoms were classified into

7 categories as shown. Original Yallourn lignite have more aromatic carbons bound to oxygen (phenolic-OH), oxygen functional groups C=O, COOH and other bond (-O-CH₂-), but less methylene bridges and terminal CH₃ content when compared with those of Taiheiyo subbituminous and Miike bituminous coal. After the reaction, decreasing of methylene bridges in the Yallourn treated coal was the lowest by less 5 %. In contrast, Taiheiyo and Miike coal showed more reduction of methylene bridge. The Yallourn treated coal have more aromatic carbons bound to oxygen and oxygen containing functional groups than those of products from others. These results indicated that the improvement of extractability of Taiheiyo and Miike coal was ascribed to the cleavage of methylene and other bridges in their coal, while lower extractability of Yallourn treated coal was caused by small cleavage of methylene bridge and a significant amount of oxygen containing functional groups.

4. CONCLUSIONS

1. Solubilization of higher-rank coals, Miike bituminous coal, by any reaction conditions was almost higher than those of lower rank coals.
2. Solubilization of lignite, Yallourn coal, depend upon reaction conditions, it was greatly changed by the stabilizer and reaction temperature.
3. The reaction with toluene as stabilizer significantly solubilized even Yallourn lignite coal because of more cleavage of ether groups and deoxygenation.

5. REFERENCES

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Table 2 Reaction condition of the treated coals.

Run	Temp. (°C)	HF (g)	BF ₃ (g)	solvent	W1 (%)
Y-1	50	5.8	1.10	toluene	37
Y-2	100	5.8	1.18	toluene	44
Y-3	150	5.8	1.26	toluene	97
Y-4	150	5.8	1.24	isopentane	32
Y-5	150	5.4	1.38	H ₂	-7
T-1	50	5.10	1.38	toluene	18
T-2	100	4.92	1.28	toluene	35
T-3	150	5.8	1.39	toluene	71
T-4	150	5.5	1.38	isopentane	24
T-5	150	5.82	1.38	H ₂	-14
M-1	50	5.46	1.4	toluene	11
M-2	100	5.46	1.4	toluene	9
M-3	150	5.82	1.4	toluene	113
M-4	150	6.06	1.25	H ₂	-3

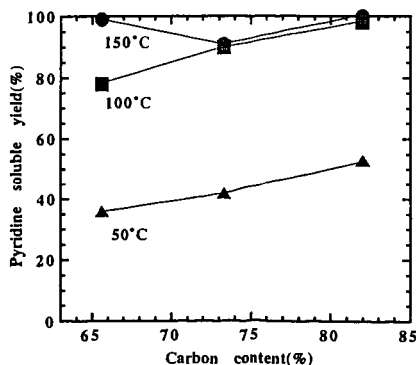


Figure 1 Effect of reaction temperature on extractability of treated coal with HF/BF₃.

Reaction condition: 3 h, toluene

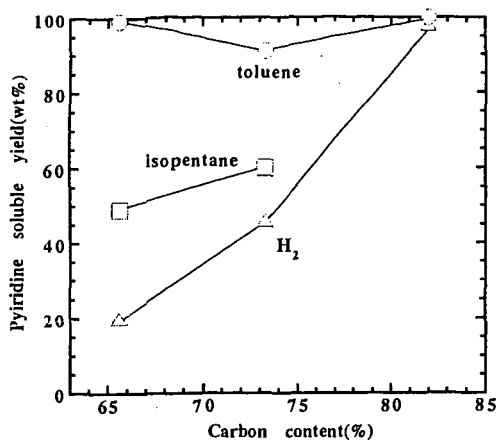


Figure 2 Effect of stabilizer on extractability of treated coal with HF/BF₃.

Reaction condition: 150°C, 3h

Table 3 Distribution of oxygen containing functional group in original coal and the treated coals.

Run	Reaction conditions				wt%				
	Temp. (°C)	HF (g)	BF ₃ (g)	solvent	COOH	OH	C=O	O _{rest}	Total
Yallourn					4.1	5.7	4.5	14.9	29.2
Y-1	50	5.8	1.10	toluene	1.9	5.0	2.8	12.8	22.5
Y-2	100	5.8	1.18	toluene	2.3	2.9	4.2	8.4	17.8
Y-3	150	5.8	1.26	toluene	0.6	1.8	4.5	6.5	13.4
Y-4	150	5.8	1.24	isopentane	0.8	3.9	4.5	9.0	18.0
Taiheiyō					0.6	5.3	3.4	9.8	19.1
T-1	50	5.10	1.38	toluene	1.0	5.1	2.8	3.7	12.6
T-2	100	4.92	1.28	toluene	0.5	6.1	2.9	3.0	12.5
T-3	150	5.8	1.39	toluene	0.7	3.4	2.8	1.7	8.6
T-4	150	5.5	1.38	isopentane	1.2	4.6	3.4	4.3	13.5
Miike					0.1	3.3	1.1	3.6	8.1
M-2	100	5.46	1.4	toluene	-	1.7	1.9	3.8	7.4
M-3	150	5.82	1.4	toluene	-	0.7	2.5	3.4	6.6

Content of oxygen functional groups and total oxygen were corrected with weight increase.

O_{rest}: ether or ester groups

Table 4 Carbon distribution in original and treated coals by NMR.

(ppm)	COOH, C=O (220-171)	Phenolic C-O (171-149)	Ar-C (149-128)	Ar-H (128-93)	-CH ₂ -O- (75-50)	-CH ₂ -CH (55-22)	-CH ₃ (22-0)
Yallourn	7.1	12.9	17.2	27.2	9.4	22.3	3.9
Y-5	8.5	14.6	18.7	26.0	6.6	18.8	6.8
Taiheiyō	4.3	8.2	15.3	24.4	7.0	34.1	6.7
T-5	3.7	9.6	18.4	29.7	7.8	22.9	7.9
Miike	4.3	8.3	15.7	24.4	5.9	32.5	8.9
M-4	3.6	10.0	21.7	31.5	6.5	18.6	8.1